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<b>(54) Title:</b> LIGHT MODULATING DEVICES INCORPORATING AN IMPROVED ELECTRODE  <b>(57) Abstract</b>  An improved light modulating device having an electrically active layer to which an electric field is applied through a pair of transparent metal electrodes. The improvement relates to providing at least one of the electrodes with a thin passivating dielectric layer to enhance degradation resistance. The dielectric layer may also act as a dielectric tuning layer.		

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## LIGHT MODULATING DEVICES INCORPORATING AN IMPROVED ELECTRODE

### Related Applications

5           This application is related to Miller et al., U.S. Serial No.  
(Applicant Docket No. 44609USA1B, filed January 10, 1992) entitled "Polymer-  
Dispersed Liquid Crystal Device Having an Ultraviolet-Polymerizable Matrix and  
a Variable Optical Transmission and Method for Preparing the Same," which is  
being filed concurrently with this application, is assigned to the same assignee as  
10       the present application, and is hereby incorporated by reference.

### BACKGROUND OF THE INVENTION

#### Field of the Invention

15           This invention relates to improved electrodes for light modulating  
devices.

#### Description of the Related Art

20           Light modulating devices are devices whose optical properties  
change in response to an electric field and return to their original condition upon  
reversing or removing the field. One example of a light modulating device is an  
electrochromic device. Such a device relies upon a reversible chemical reaction to  
cause a change in optical properties. Another example is a liquid crystal display  
device whose optical appearance changes upon application of an electric field.

25           A third example of a light modulating device is the so-called  
Nematic Curvilinear Aligned Phase ("NCAP") device described, e.g., in  
Ferguson, U.S. Patent No. 4,435,047. These devices include a liquid crystal layer  
in which nematic liquid crystal material is encapsulated in a polymer matrix. The  
encapsulated material is prepared by combining the liquid crystal material with the  
30       polymer matrix in the form of an aqueous emulsion, and then casting a film from  
the emulsion. These devices are relatively translucent in the absence of an electric

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field due to light scattering, but are relatively transparent upon application of a field.

A fourth example of a light modulating device is the Polymer-Dispersed Liquid Crystal ("PDLC") device described, e.g., in Doane et al., U.S. 4,688,900. These devices include a liquid crystal layer in which liquid crystal droplets are dispersed throughout a polymer matrix. The liquid crystal layer is prepared by combining the liquid crystal material with a polymerizable matrix precursor (e.g., one or more ultraviolet-curable monomers) and then subjecting the mixture to polymerization conditions. Polymerization causes phase separation of the liquid crystal material, resulting in the formation of liquid crystal droplets dispersed throughout the polymerized matrix. Like the NCAP devices, the PDLC devices are translucent in the field-off condition due to scattering and transparent in the field-on condition.

All of the above-described light modulating devices require transparent electrodes on at least one side of the electrically active layer to apply the electric field. The electrode on the other side may be transparent or opaque. Suitable transparent electrodes generally fall into two classes.

The first class includes degenerate semiconductors that are non-metallic transparent conductors such as indium-tin oxide (ITO) and tin oxide. The NCAP devices described in Fergason, U.S. Patent No. 4,435,047 use such electrodes. These electrodes have the advantage of exhibiting high transmission and low reflection of visible light. They are also relatively stable against chemical degradation due, e.g., to the liquid crystal layer; thus, it may not be necessary to provide them with additional protection. However, their conductivity and solar control (i.e., the extent to which the electrode blocks transmission of non-visible light by reflection or absorption) is less than optimal for some applications.

The second class includes metallic conductors such as silver which are transparent when applied as thin films. Such electrodes have the advantage of exhibiting high conductivity and good solar control. The higher conductivity of these conductors allows the construction of large area displays with a partially conductive electrically active material. However, they are susceptible to chemical,

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thermal, and ultraviolet degradation, thereby limiting device lifetime. In addition, their transmission and reflection properties are less than optimal.

It is known to provide metal films (e.g., silver films) with an overcoating of a dielectric film to protect the metal surface from chemical and physical attack. In such applications, however, the metal film is not being used to apply an electric field. For example, Hass et al., Applied Optics, 14(11):2639-44 (1975) describes silver mirrors coated with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_x$  films to protect the silver metal from tarnishing due to sulfide and moisture attack, while at the same time maintaining the reflectance properties of the metal.

It is also known that application of a dielectric film to a metal film can change the optical properties of the underlying metal film. For example, Kusano et al., J. Vac. Sci. and Tech., A 4(6):2907-10 (1986) describes transparent heat reflective films of, e.g., zinc oxide and silver in which the silver layer reflects infrared radiation and the oxide layer suppresses reflection of visible light. Sainty et al., Appl. Optics, 23(7):1116-19 (1984) notes that dielectric films deposited on metal films can perform the dual function of protecting the metal from the environment and enhancing its optical performance (e.g., by altering its reflectivity properties). In neither case, however, were the metal films being used to apply an electric field.

Van Konynenburg et al., SPIE vol. 823 Optical Materials Technology for Energy Efficiency and Solar Energy Conversion VI, pp. 143-50 (1987) describes a window for controlling solar radiation that incorporates a layer of NCAP liquid crystal material. One of the electrodes is said to be "low-emissivity" glass. Its composition, however, is not specified further.

Ferguson, U.S. Patent No. 4,810,063 describes an NCAP device in which the back surface of the substrate supporting the liquid crystal layer (i.e., the surface furthest from the liquid crystal layer) contains a "tuned" dielectric coating. Examples of suitable coatings include lithium fluoride and barium oxide. The purpose of the coating is to effect selective constructive and destructive optical interference in order to enhance illumination in the field-off state. The coating, however, is not applied to the electrodes (which are described as being indium-tin oxide, tin oxide, antimony-doped tin oxide, or electrically conductive ink).

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SUMMARY OF THE INVENTION

In general, the invention comprises a light modulating device comprising an electrically active layer (i.e., a layer whose optical properties change in response to an applied electric field) to which an electric field is applied through a pair of metal electrodes, at least one of which is transparent, wherein at least one of the electrodes further comprises a thin passivating dielectric layer interposed between the electrode and the electrically active layer to enhance the degradation resistance (e.g., resistance to chemical, thermal, moisture, and ultraviolet light induced degradation) of the electrode. The dielectric passivating layer (i.e., a layer made of a material having less than 10% optical light absorption and an electrical conductivity less than  $1 \times 10^4$  mho/cm.) is preferably applied to both of the electrodes in the light modulating device. In this way, the lifetime of the electrode, and thus the device, is extended. Where both electrodes are provided with a dielectric layer the dielectric layer of each electrode may be the same as or different from the dielectric layer of the other electrode. A thicker, substantially opaque metal electrode may also be protected with a dielectric layer.

Corrosive chemical components of the electrically active layer are the cause of the metal electrode degradation but the rate of degradation can be influenced by environmental factors such as heat, moisture, and ultraviolet radiation. Metal electrodes provided with a thin dielectric passivating layer afford protection where the electrically active layer is an electrochromic material (e.g., tungsten oxide), a liquid crystal material, a PDLC material, or an NCAP material.

By choosing a dielectric layer having an appropriate refractive index and thickness (relative to the refractive index and thickness of the both the electrically active and metal layers), the dielectric layer can provide the additional benefits of a tuning layer to increase transmission and decrease reflection of the device upon application of an electric field. Where the device is incorporated, e.g., in a window for architectural or automotive applications, it is preferred that the refractive index and thickness be chosen to increase transmission and decrease reflection at a wavelength of 550 nanometers (nm), which is approximately the midpoint of the visible spectrum. By maximizing transmission and minimizing reflection, glare is reduced and the visual appearance of the window is improved.

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Where the tuning function is desired, the refractive index of the dielectric layer should lie between the index of the electrically active layer and the electrode. The refractive index of a metal electrode is effectively very high (typically greater than 2) thus, the refractive index of the electrode acts as an upper limit for the refractive index of the dielectric layer. In the case of non-isotropic PDLC and NCAP layers, the refractive index of the layer for this purpose is considered to be the average of the refractive index of the polymer matrix and the ordinary and extraordinary refractive indices of the liquid crystal material. The larger the difference in refractive index between the dielectric layer and the electrically active layer (with the refractive index of the metal electrode acting as the upper limit), the more pronounced the tuning effect. In general, the difference should be at least 0.2. For many useful electrically active layers, this requirement is satisfied by choosing a dielectric layer having a refractive index of at least 1.9.

The device can also be constructed so that it appears colored (instead of clear) upon the application of an electric field. This can be achieved, e.g., by choosing a dielectric layer which is inherently colored by selective absorption in the visible light region. Alternatively, the refractive index and thickness of the dielectric layer can be selected to achieve color. In addition, the metal electrode itself can consist of a composite structure that includes one or more metal and dielectric layers (in addition to the dielectric layer in contact with the electrically active layer). An example of such a composite would be an electrode consisting of a dielectric layer sandwiched between two metal layers.

Because of its optimal electrical and solar control properties, silver is the preferred material for the metal electrode. Other suitable metals include gold, copper, aluminum, titanium, chromium, iron, nickel, and alloys thereof. Preferred materials for the dielectric layer (especially where the device is to be used in a window) are those which do not substantially absorb light in the visible spectrum (i.e., wavelengths between 400 and 800 nm). Suitable materials include metal oxides, sulfides, halides, and combinations thereof. Metal oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$ , indium-tin oxide (ITO),  $\text{ZnO}$ ,  $\text{CeO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ , and  $\text{TiO}_2$  are particularly useful.

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It is important that the material chosen for the dielectric layer, its thickness, and its method of deposition be chosen such that the electrical conductivity or optical properties of the electrode is not materially degraded by its application. The electrical conductivity of the electrode after application of the dielectric layer is at least 0.001 mhos/sq., preferably 0.1 mhos/sq. The dielectric layer is designed to protect the metal from degradation to ensure that this level of conductivity is maintained. As will be explained more fully in the Detailed Description of the Preferred Embodiments, it is desirable that at least 50%, and preferably at least 75%, of the electrical conductivity of the protected electrode is retained following exposure for 20 weeks to a water bath chamber incorporating a 24 hour, 50% duty cycle ultraviolet sunlamp.

It is also important that the dielectric layer adhere well to the electrically active layer to maintain electrical contact and to prevent the formation of visual defects (e.g., gaps) due to delamination. Preferably, the force required to separate the dielectric layer from the electrically active layer (by pulling the electrodes away from the electrically active layer) is at least 100 gm/2.54 cm (100 gm/in) in a 180° Peel test.

The shading coefficient is a measure of the degree of solar control the device exhibits. As will be explained more fully in the Detailed Description of the Preferred Embodiments, it is calculated by comparing the amount of solar energy entering a window provided with the light modulating device to that of a window without the device. In general, the lower the value of the shading coefficient, the greater the amount of solar energy that is rejected by the window (i.e., by absorption or, more preferably, reflection) in the presence of an electric field. By providing the electrodes with thin dielectric passivating layers, the shading coefficient of a window provided with the device preferably is no greater than 0.5 in the field-on state.

The invention provides a light modulating device which takes advantages of the benefits transparent metal electrodes offer over non-metallic electrodes such as indium-tin oxide (e.g., superior solar control and electrical conductivity), while protecting the electrodes against degradation which, until now, has limited practical use of metal electrodes in light modulating devices. In



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addition, by careful choice of refractive index and thickness, the dielectric layer can be made to perform the dual function of protecting the underlying metal electrode and tuning incoming light to maximize transmission and reduce reflection in the presence of an electric field (thereby reducing glare). These features make  
5 light modulating devices incorporating such protected metal electrodes particularly useful in windows for architectural and automotive applications.

Other features and advantages of the invention will be apparent from the following Detailed Description of the Preferred Embodiments thereof, and from the claims.

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#### BRIEF DESCRIPTION OF THE DRAWING

The invention will be more fully understood with reference to Figure 1 which is a schematic view, partially in cross-section, of a PDLC device incorporating the electrode of the present invention.

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#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to a transparent or opaque metal electrode (i.e., transparent to light in the visible spectrum) provided with a thin, protective, passivating, dielectric layer which is useful in a variety of light modulating  
20 devices. Known light modulating devices include devices in which the electrically active layer (i.e., the layer whose optical properties change upon application of an electric field) is an electrochromic, liquid crystal, PDLC, or NCAP material. In all of these devices, the metal electrode is susceptible to chemical attack by the components of the electrically active layer, as well as attack by environmental  
25 factors such as heat, moisture, and ultraviolet radiation. For example, electrochromic devices based upon, e.g., tungsten oxide, typically rely in part on the movement of hydrogen ions to effect an optical change. However, when these ions contact the metal electrodes, corrosion may result. In the case of liquid crystal, PDLC, and NCAP layers, the liquid crystal material itself may be  
30 corrosive. The PDLC and NCAP layers suffer from an additional disadvantage in this regard in that the polymer matrix may also attack the electrode.

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The invention is particularly useful in PDLC devices. Examples of preferred PDLC devices and a method for preparing them are described in the related Miller et al. U.S. patent application, referred to above. These devices typically use metallic silver electrodes, although gold, copper, aluminum, titanium, chrome, iron, and nickel (and alloys thereof) may also be used. Silver is a particularly desirable electrode material in applications involving windows because it exhibits good electrical conductivity (e.g., about  $7 \times 10^5$  mhos/cm compared to less than  $5 \times 10^3$  mhos/cm for indium-tin oxide) and solar control, as measured by the shading coefficient (which will be described in more detail below). In spite of these advantages, however, the utility of silver metal electrodes is limited because the silver metal is prone to attack by both the liquid crystal material and the polymer matrix. This is particularly true where the PDLC matrix is, for example, a UV-curable thiol-ene matrix, as described in the co-pending Miller et al. application referred to above. In the case of the thiol-ene matrix, unreacted mercaptan moieties may attack and chemically degrade the silver metal electrode. Providing a thin passivating dielectric layer on top of the electrode protects against such attack.

The light modulating devices described in the Miller et al. application referenced above display positive dielectric anisotropy wherein the liquid crystal materials in the PDLC film align when a current is applied to the device and the device becomes transparent. The electrodes of the present invention are equally adaptable to light modulating devices displaying negative dielectric anisotropy wherein the liquid crystal materials are aligned and the device is transparent in the field-off state and the device becomes opaque in the field-on state. The discussion herein generally describes passivating dielectric layers in context of devices displaying positive dielectric anisotropy, and appropriate modifications of the described parameters to devices displaying negative dielectric anisotropy will be readily apparent to the skilled artisan.

An example of a thin film PDLC device 10 incorporating the electrode of the present invention is shown in Figure 1. In this embodiment, the device 10 comprises a PDLC film 12 having a multiplicity of liquid crystal droplets 14 dispersed in a polymeric matrix 16. First and second flexible

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substrates 18 and 20 carry thin film metal electrodes 22 and 24 which, in turn, are coated with thin passivating dielectric layers 26 and 28. Substrates 18 and 20 form a sandwich with PDLC film 12, with passivating layers 26 and 28 contacting the PDLC film 12. Electrodes 22 and 24 are thus protected from degradation as the PDLC directly contacts the passivating layers which provide a barrier, protecting the electrodes from potentially corrosive materials in the PDLC film 12.

A variety of materials can be used for flexible substrates 18 and 20, including polyethylene terephthalate (PET), copolyesters, polyether sulfones, polyimides, poly(ethylene naphthalate), poly(methyl methacrylate), and polycarbonate. PET is the preferred material.

Electrodes 22 and 24 of PDLC device 10 are connected to an alternating current (AC) power supply 34 having a variable voltage output through leads 30 and 32. The frequency of the alternating field should preferably be in the range of 40 to 100 hertz. The field should alternate sufficiently rapidly so that a human observing the device in a field-on state would not perceive flickering.

Regardless of the type of light modulating device, there are several basic requirements which the dielectric layer must meet in order to be useful. First, the thickness and density of the layer must be such that the layer can act as a barrier against diffusion of chemical species from the electrically active layer to the electrode as well as serving as a barrier against the environment. However, it must be thin enough so that it does not significantly diminish the electric field applied to the electrically active layer.

The specific values for the density and thickness will depend on the particular dielectric material and electrically active material used. In general, it should be a quarter wavelength of optical thickness. The quarter wavelength dimension is determined by depositing a dielectric material onto the electrode at a thickness such that it maximizes the transmission and minimizes the reflection of incident light. The quarter wavelength thickness for a given dielectric material will vary depending on the metal used in the electrode. Because of the decrease of the electrical field across the electrically active layer, the thickness of each dielectric layer preferably is no greater than 10% of the thickness of the

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electrically active layer. In a typical PDLC device, this translates to a thickness of between about 5 and 2000 nm.

A second requirement is that both the dielectric material and its method of deposition must be compatible with the underlying electrodes. By "compatible" it is meant that neither the material itself nor the method used to deposit it on the electrode will materially degrade the electrical and optical properties of the electrode. For example, often the oxide deposition process, particularly where the oxide is sputter-coated onto the electrode, heats or oxidizes the metal electrode, thereby reducing electrical conductivity.

A third requirement is that the dielectric layer must be substantially optically passive in the performance of the device, except when this layer is selected to provide color.

A fourth requirement is that the dielectric layer must adequately adhere to both the underlying metal electrode and to the electrically active layer.

If adhesion is not adequate, electrical contact between the electrode and the electrically active layer will be lost. Delamination will also cause visual defects upon switching due to reduced field strength across the electrically active area corresponding to the delaminated areas. Visual defects in the device may also be apparent in the field-off state due to the presence of air, which has a low index of refraction, between the metal electrode and the electrically active layer.

The peel strength is a measure of the force necessary to separate the two sets of electrodes with the electrically active material between them. For devices having at least one flexible substrate, peel strength is measured by a 180° peel test using an Instrumentors Slip/Peel Tester at a rate of 15.2 cm/min (6 inches/min). For example, PDLC devices having proper droplet formation and cure generally show an adhesive failure between the dielectric layer and the electrically active layer. Preferably, the peel force should be at least 100 gm/2.54 cm (100 gm/in) in PDLC or NCAP devices. The second most common failure mode is an adhesive failure between the substrate and the deposited metal, with the adhesion between the dielectric and the metal electrode being the greatest.

The ability of a single dielectric material to offer the barrier properties, the optical properties, the adhesive properties and the materials

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compatibility properties without significantly diminishing the electrical field applied to the electrically active layer was a surprising discovery. Remarkably, the dielectric layer did not impair the ability to make an electric connection between the electrode and the power supply through the dielectric layer. The dielectric layer actually affords protection for the electrode from chemical attack from adhesive electrical connectors. Even more surprising was the fact that several dielectric materials were identified which were able to produce the desired balance in properties.

In addition to providing protection against degradation, a dielectric layer may also be chosen which enhances the optical properties of the device. For example, the optical thickness of the dielectric layer is the product of its refractive index times its physical thickness. The optical thickness of the dielectric layer affects the transmission and reflection properties of the device. By choosing a dielectric layer having a refractive index sufficiently larger than the refractive index of the electrically active layer, the dielectric layer acts as an optical "tuning" layer to maximize transmission and minimize reflection of visible light upon application of an electric field. Such characteristics are particularly useful in applications involving windows because they improve optical clarity by reducing glare. In such applications, it is desired to maximize transmission and minimize reflection at 550 nm.

It is also possible to achieve some tuning effect with a small difference in refractive index. However, it is preferred to maximize the refractive index difference if tuning is desired. In the case of PDLC materials described by Miller et al., an adequate differential is achieved by choosing a dielectric layer whose refractive index is at least 1.9 (and preferably 2.0 or greater).

The thickness of the dielectric layer for tuning applications will depend on the dielectric material as well as the composition of the electrically active layer. Generally the thickness of the dielectric layer is between 25 and 100 nm in order to take advantage of both the protective ability of the layer and the tuning effect.

The dielectric layer may also be used to impart color to the device if the optical transmission and reflection of the resulting device in the visible light

range vary with wavelength. This may be achieved by using a dielectric layer that is inherently colored by absorption, by using a single layer of sufficiently high index, or by using multiple dielectric or metal layers. If multiple metal layers are used, tuning may be achieved by using a half-wave thickness of dielectric material between the metal layers in a metal-dielectric-metal (MDM) construction. The innermost metal electrode would be protected from the electrically active layer with an additional dielectric protective layer.

The use of a transparent metal electrode improves the solar control of the light modulating devices. Solar control refers to the ability of the device to transmit visible light while blocking radiation from other portions of the spectrum (e.g., infrared radiation). Blocking is accomplished by either absorbing or reflecting the undesired radiation, with reflection being preferred.

The degree of solar control exhibited by a device can be represented by its shading coefficient. The shading coefficient ( $S_c$ ) is the ratio of the amount of solar energy that enters a window equipped with the light modulating device compared to the amount that enters a clear 1/8 inch thick glass pane. The lower the value of shading coefficient, the greater the amount of solar energy that is blocked. The shading coefficient is calculated according to the following equation:

$$S_c = \frac{T_{sf} + A_{sf}(R)}{T_{sg} + A_{sg}(R)}$$

Where  $S_c$  is the shading coefficient;

$T_{sf}$  is the solar transmission of the window equipped with a light modulation device;

$T_{sg}$  is the solar transmission of the glass pane;

$A_{sf}$  is the solar absorption of the window equipped with a light modulation device;

$A_{sg}$  is the solar absorption of the glass pane; and

$R$  is a weighting factor that varies with the window application.

The Air Mass 2 solar spectrum was used for calculating shading coefficients.

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Basically,  $R$  is a measure of the relative amount of solar energy that is absorbed by the window and subsequently conducted into the interior less the amount of absorbed energy that is removed from the window by convection and conduction to the exterior. This balance between interior and exterior energy gain and loss is a function of the angle of the glass and the air flow over the glass. For common window glass in a vertical configuration with no air flow,  $R$  is approximately 0.25,  $T_{sg}$  is 92%, and  $A_{sg}$  is 0%. (see ASHRAE Handbook of Fundamentals, Chapter 27, p. 27.24. (1989).

Use of a passivating dielectric layer allows the practical use of metal electrodes with decreased solar energy transmission and increased solar reflection, resulting in a decreased shading coefficient. Preferably, shading coefficients of less than 0.5 are obtained. In the case of PDLC and NCAP devices, which rely on light scattering in the field-off state to achieve translucency and alignment of the liquid crystal in the on-state to increase clarity, the shading coefficient is slightly greater in the field-on state compared to the field-off state.

As is apparent from the above discussion, the choice of the particular material for the passivating dielectric layer will depend on the function the layer is to perform (e.g., protection against degradation only or a combination of protection and tuning), as well as the particular material forming the electrically active layer. In general, suitable materials are based upon metal oxides (e.g.,  $HfO_2$ ,  $Y_2O_3$ ,  $ZrO_2$ ,  $Pr_6O_{11}$ ,  $Sc_2O_3$ ,  $SiO$ ,  $Sb_2O_3$ ,  $Bi_2O_3$ ,  $SiO_2$ ,  $Ta_2O_5$ ,  $TiO_2$ ,  $ThO_2$ , and particularly  $Al_2O_3$ ,  $SnO_2$ , ITO,  $ZnO$ ,  $CeO_2$ ,  $Ta_2O_5$ ,  $ZrO_2$ , and  $TiO_2$ ), sulfides (e.g.,  $ZnS$ ), halides (e.g.,  $AgCl$ ,  $MgF_2$ ), solution or vapor coated organic polymers, or combinations thereof. In the case of PDLC devices,  $Al_2O_3$  is preferred when a protection-only layer is desired, whereas  $SnO_2$  is preferred for both protection and tuning (there being a greater refractive index difference between  $SnO_2$  and most PDLC materials compared to the difference exhibited using  $Al_2O_3$ ).

The passivating dielectric layers are generally applied to the metal electrode using standard thin film deposition techniques. These techniques include vacuum evaporation, sputter coating, cathodic arc deposition, spray pyrolysis and chemical vapor deposition. The particular deposition technique, as well as the

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deposition conditions (e.g., temperature, reactive gas pressure, etc.), are a function of the particular materials used for the device (i.e., dielectric material, metal electrode, and electrically active material).

5 The invention will be more fully understood with reference to the following examples which are not to be construed as limiting the scope of the invention.

#### General Preparation of Electrodes

10 Preparation and characterization of the electrodes of the present invention are described below.

Silver electrodes were prepared by vacuum deposition on a 25 $\mu$  PET substrate in a vacuum webcoater by both evaporation and sputtering techniques. For vacuum evaporation of silver, a resistively heated Ag source contained in a boron nitride crucible was evaporated onto a free span web moving at a speed of 12.2 m/min (40 ft/min). For sputtered silver, a metal target was magnetron sputtered onto a free span web moving at a speed of 4.6 m/min (15 ft/min) using argon as the sputtering gas at 5 $\mu$  pressure. The power levels applied to the metal sources were chosen to deposit silver layers having a thickness giving rise to transmission levels of 60%, 55%, 50%, and 45% as measured at 550 nm wavelength. The approximate thickness for these silver films were 12.0 nm, 13.2 nm, 14.6 nm, and 16.8 nm, respectively as calculated from optical properties of the coated electrodes.

25 A passivating dielectric layer of SnO<sub>2</sub> was sputter coated on a 50% transmission silver film and on a 45% transmission film by means of a reactive magnetron sputtering process onto a web cooled with a chill roll. The sputtering gas composition was a uniform mixture produced by combining a flow of 70 standard cubic centimeters (sccm) oxygen and 100 sccm argon. A passivating dielectric layer of Al<sub>2</sub>O<sub>3</sub> was reactively evaporated on a 60% transmission silver film and on a 50% transmission film from a resistively heated alumina crucible containing Al metal. Oxygen, maintained at a flow rate of 470 sccm, which resulted in a pressure of 7x10<sup>-4</sup> torr, was used as the reactive gas in the reactive deposition processes. The thickness of the films was chosen to provide the dual

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function of degradation resistance and maximizing transmission at 550 nm. For the  $\text{SnO}_2$  films the thickness was about 35 nm, while in the case of the  $\text{Al}_2\text{O}_3$  films it was about 45 nm. Indium-tin oxide electrodes (ALTAIR-0-30, 7 mil PET) were purchased from Southwall Technologies, Palo Alto, CA.

- 5                   Metal-Dielectric-Metal (MDM) electrodes were prepared by sputter coating a first layer of Ag, approximately 13 nm thick on a PET backing (25  $\mu$  thick) followed by reactively evaporating a layer of  $\text{Al}_2\text{O}_3$  dielectric approximately 90 nm thick, which corresponded to a half wave length separation at 530 nm, and then sputter coating a second layer of Ag approximately 17 nm  
10 thick over the  $\text{Al}_2\text{O}_3$  layer. The second, or outermost, layer of Ag was protected from the PDLC film by a dielectric protective layer of  $\text{Al}_2\text{O}_3$ .

- Optical measurements (i.e., % visible transmission, % visible reflection, % solar transmission, and % solar reflection) were measured using a Perkin Elmer Lambda 9 spectrophotometer having an integrating sphere. All  
15 measurements were made in the absence of an applied electric field. Samples were placed directly on ports of the integrating sphere so total transmission and reflection were measured. The results of the optical measurements are reported in Table 1 where "T" refers to transmission and "R" refers to reflection.

Table 1

## Optical Properties of Electrodes before PDLC Coating

Example	Electrode	Visible T (%)	Visible R (%)	Solar T (%)	Solar R (%)
C - 1	77%T ITO/PET	77.5	14.6	75.4	14.3
C - 2	60%T Ag/PET	65	26	47	42
C - 3	50%T Ag/PET	50	38	35	53
1	Al <sub>2</sub> O <sub>3</sub> /60%T Ag/PET	78.5	11.8	58.5	32
2	Al <sub>2</sub> O <sub>3</sub> /50%T Ag/PET	71.1	19.5	49.9	42
3	SnO <sub>2</sub> /45%T Ag/PET	68.5	20	45.3	45.9
4	SnO <sub>2</sub> /55%T Ag/PET	78.2	11.2	54.4	35.5
5	Al <sub>2</sub> O <sub>3</sub> /MDM/PET	64.1	8.4	41.3	35.4

The results shown in Table 1 demonstrate that incorporation of a thin layer of a dielectric passivating material, as seen with Examples 1 - 5, resulted in enhanced optical properties relative to the uncoated silver films, with visible transmission values approaching that of indium-tin oxide (ITO) sample (C - 1) and reflection lower than the uncoated materials (C - 2 and C - 3).

The electrical conductivity of the electrodes prepared in Example 1 was also measured using an LEI contactless conductivity probe, the results of which are reported in Table 2.

Table 2

Electrical Conductivity of Electrodes before PDLC Coating

Example	Electrode	Conductivity (mhos/sq.)
C - 1	77%T ITO/PET	<0.02
C - 2	60%T Ag/PET	0.1
C - 3	50%T Ag/PET	0.25
1	Al <sub>2</sub> O <sub>3</sub> /60%T Ag/PET	0.1
2	Al <sub>2</sub> O <sub>3</sub> /50%T Ag/PET	0.25
3	SnO <sub>2</sub> /45%T Ag/PET	0.3
4	SnO <sub>2</sub> /55%T Ag/PET	0.2
5	Al <sub>2</sub> O <sub>3</sub> /MDM/ PET	0.30

The electrical conductivity results show that the conductivity of electrodes coated with a passivating dielectric material (Examples 1 and 2) does not change substantially from that of the uncoated silver electrodes (Examples C - 2 and C - 3). All of the metal electrodes had substantially higher electrical conductivities than indium-tin oxide (Example C - 1).

#### General Preparation of a PDLC Device

Light modulating devices in which the electrically active layer was a PDLC film were prepared using the electrodes prepared in Example 1. They were prepared using the techniques disclosed in Miller et al., U.S. Serial No.

(Applicant Docket No. 44609USA1B, filed January 10, 1992). In general, the method of preparation is as follows. Equal parts by weight of LICRISTAL E7 (available from EM Industries, Hawthorne, NY) and NOA65 (a thiol-ene based

matrix material available from Norland Products, Inc., New Brunswick, NJ) were heated to approximately 60°C, with mixing, until the liquid crystal material completely dissolved. The liquid crystal/uncured polymer matrix material blend was poured between a pair of 25 micron thick polyester films which previously had been coated with a transparent electrode (with or without a protective passivating material coating) on one surface of each film. The two films were held with their electrode coated surfaces in facing relationship by the nip rollers of a precision two roll nip coater. The gap between the nip rollers was set to provide a liquid crystal material/uncured polymer matrix material film thickness of 15 to 21 microns.

Other commercially available liquid crystal materials useful in preparing PDLC devices which utilize the electrodes of the present invention include LICRISTAL BL006, BL009, BL036, BL038, ML1005, ML108, 17151, 17153, and 17315, all available from EM Industries, Hawthorne, NY).

Another thiol-ene based polymer matrix material useful in preparing PDLC devices which utilize the electrodes of the present invention is NOA 68, available from Norland Products, Inc. New Brunswick, NJ).

The polymer matrix was polymerized by positioning the sandwichlike construction comprising the two electrode coated substrates and the liquid crystal material/uncured matrix material between a pair of opposed banks of fluorescent black light phosphor lighting elements, each bank being positioned to illuminate one of the polyester films. Lighting elements having a spectral distribution between 300 and 400 nm and a maximum output at 351 nm were employed.

The lighting elements were adjusted so as to provide an average intensity of 1.1 mW/cm<sup>2</sup> through each electrode coated polyester film. Each side of the sandwichlike construction received a total energy exposure of 100 mJ/cm<sup>2</sup>. The construction as a whole was exposed to a total energy of 200 mJ/cm<sup>2</sup>. The average intensity for sample 8 was 0.5 mW/cm<sup>2</sup> with a total exposure of 330 mJ/cm<sup>2</sup>. The level of incident radiation was determined with an EIT low intensity UVIMAP radiometer having a spectral response in the range of 300 to 400 nm with maximum transmission at 358 nm.

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Electrically conductive adhesive tape (i.e. 3M 9703 z-axis conductive tape placed on 3M 1181 copper foil tape) was secured to a portion of each electrode coated substrate along an edge that had not been previously coated with liquid crystal/matrix material. Each tape was subsequently connected to an alternating current (AC) power supply having a variable voltage output so that the device could be switched between a field-on and field-off state.

The optical properties of the devices were measured using the same procedure described for measuring the optical properties of the electrodes except that the optical measurements were made with the device in the field-off state. In the case of reflectance measurements, separate measurements were made for the top and bottom of the device (because the electrodes used in the devices had different compositions, their reflectance properties are expected to be different). The results are shown in Table 4. The shading coefficients for each device were calculated and the results are shown in Table 4.

Table 3  
PDLC Device Electrode Configurations

Example	Electrode A Example #	Electrode B Example #
C - 4	C - 1	C - 1
C - 5	C - 2	C - 3
6	1	2
7	5	1
8	4	5

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Table 4

Optical Properties of PDLC Devices

Example	Side	Visible T (%)	Solar T (%)	Visible R (%)	Solar R (%)	Shading Coefficient
C - 4	A	68.1	82.1	14.6	13.7	0.9
	B	68.1	82.1	14.6	13.7	0.9
C - 5	A	28.4	20.4	39.4	49.7	0.3
	B	28.4	20.4	43.4	54.6	0.29
6	A	28.8	20.8	40.6	50.5	0.3
	B	28.8	20.8	44.3	55.8	0.29
7	A	25.8	13.9	25.1	53.7	0.24
	B	25.8	13.9	34.6	49.3	0.25
8	A	38.4	23.8	26.8	44.8	0.34
	B	38.4	23.8	31.6	51.2	0.33

The results shown in Table 4 demonstrate that PDLC devices prepared using thin, passivating dielectric layers can exhibit enhanced optical properties (i.e. 7 and 8).

Electrode stability was measured in a noncondensing, water bath chamber exposed to a 24 hr, 50% duty cycle of UV Sunlamps, GE type RSM-6. Stability of electrodes was measured by monitoring conductivity of the electrodes with a LEI contactless conductivity probe which measured the sheet conductivity of the electrodes and not the conductivity of the PDLC matrix. Any reaction of corrosive components in the PDLC film with the Ag electrodes decreased the conductivity of the electrode. Protected and unprotected electrodes, as indicated, were used to make PDLC and control samples with the following liquid crystal/polymer matrix mixtures: E7/NOA65, BL009/NOA65, and pure NOA65. In their first 20 weeks of exposure to the artificial sunlight, temperature, and humidity cycling, protected electrodes showed better retention of their conductivity than unprotected electrodes. Aluminum oxide or tin oxide layers between the metal electrodes and the PDLC layer do protect the thin film Ag electrodes from

corrosion under the test conditions. After a small initial decrease in conductivity, many passivated samples show little or no change with increasing exposure to the environmental chamber.

Conductivity measurements of the devices at the beginning and end of a 20  
5 week environmental stability study test are reported in Table 6. The data  
demonstrate that on weathering, PDLC devices containing the liquid crystal E7 are  
subject to the largest drop in conductivity, those containing the liquid crystal  
BL009 are subject to intermediate conductivity losses, and devices containing no  
10 liquid crystal materials are the most stable under the conditions studied.

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Table 6  
Weathering/Conductivity Stability Studies

Example	Electrode A/B Exam.#'s	Electrically Active Material	Matrix Material	Beginning Conductivity (mhos/sq.)	Final Conductivity (mhos/sq.)	Final Conductivity (% of original)
C - 6	C-2/C-3	BL009	NOA 65	0.36	0	0
9	1/2	BL009	NOA 65	0.36	0.29	81
10	3/4	BL009	NOA 65	0.44	0.4	91
C - 7	C-2/C-3	E7	NOA 65	0.36	0	0
11	1/2	E7	NOA 65	0.36	0.27	75
12	3/4	E7	NOA 65	0.44	0.36	82
C - 8	C-2/C-3	-	NOA 65	0.36	0.15	42
C - 9	1/2	-	NOA 65	0.36	0.36	100



180° Peel Strength measurements of the above PDLC devices were determined according to the previously described test procedure and are reported in Table 7.

5

Table 7  
Peel Strength of PDLC Devices  
With and Without Dielectric Protected Electrodes

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Example	Electrode A/B Exam. #'s	Electrically Active Material	Matrix Material	Peel Strength (gm/in.)
C - 6	C-2/C-3	BL009	NOA 65	>500
9	1/2	BL009	NOA 65	320
10	3/4	BL009	NOA 65	228
C - 7	C-2/C-3	E7	NOA 65	165
11	1/2	E7	NOA 65	>500
12	3/4	E7	NOA 65	162
C - 8	C-2/C-3	-	NOA 65	263
C - 9	1/2	-	NOA 65	491

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Reasonable variations or modifications are possible within the scope of the foregoing specification and drawings without departing from the spirit of the invention which is defined in the accompanying claims.

25

CLAIMS

The embodiments for which an exclusive property or privilege is claimed are defined as follows:

- 5           1. A light modulating device comprising an electrically active layer to which an electric field is applied through a pair of metal electrodes, at least one of said electrodes being transparent, wherein at least one of said pair of electrodes further comprises a thin passivating dielectric layer interposed between said electrode and said electrically active layer to enhance the degradation resistance of  
10   said electrode.
2. The device of claim 1 wherein said electrically active layer comprises a layer of PDLC material.
3. The device of claim 1 wherein said electrically active layer comprises a layer of material comprising liquid crystals.
- 15          4. The device of claim 1 wherein said electrically active layer is an electrochromic material.
5. The device of claim 1 wherein both of said electrodes are provided with a thin passivating dielectric layer to enhance degradation resistance.
6. The device of claim 1 wherein the refractive index and thickness  
20   of said dielectric layer are chosen to increase transmission and decrease reflection by said device in the presence of an electric field.
7. The device of claim 6 wherein the difference between the refractive index of said dielectric layer and the refractive index of said electrically active layer is at least 0.2.
- 25          8. The device of claim 1 wherein the material for said metal electrode is chosen from the group consisting of silver, gold, copper, aluminum, titanium, chromium, nickel, iron, and alloys thereof.
9. The device of claim 1 wherein said dielectric layer does not substantially absorb light in the visible region.
- 30          10. The device of claim 1 wherein said dielectric layer is chosen from the group consisting of metal oxides, sulfides, halides, and combinations thereof.

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11. The device of claim 1 wherein the electrical conductivity of said electrode provided with said dielectric layer is at least 0.001 mhos/sq.

12. The device of claim 1 wherein the shading coefficient of said device is less than 0.5.

5 13. The device of claim 1 wherein at least 50% of the electrical conductivity of said electrode provided with said dielectric layer is retained following exposure for 20 weeks to a water bath chamber incorporating a 24 hour, 50% duty cycle ultraviolet sunlamp.

10 14. A light modulating device comprising an electrically active PDLC layer to which an electric field is applied through a pair of transparent silver electrodes, both of said electrodes being provided with a thin passivating dielectric layer interposed between the electrode and the PDLC layer to enhance degradation resistance, said dielectric layer being chosen from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$ , indium-tin oxide,  $\text{ZnO}$ ,  $\text{CeO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ , and  $\text{TiO}_2$ .

15 15. A light modulating device comprising an electrically active layer to which an electric field is applied through a pair of metal electrodes, at least one of said electrodes being transparent, wherein at least one of said pair of electrodes further comprises a thin passivating dielectric layer interposed between said electrode and said electrically active layer to enhance the degradation  
20 resistance of said electrode, said light modulating device further comprising an alternating current power supply.

16. A method of producing a light modulating device having thin metal electrodes with improved resistance to corrosive contaminants, said method comprising the steps of:

25 applying a thin coating of a passivating dielectric material over said metal electrode;

forming a layered construction having an electrochemically active material contained between a pair of electrodes, at least one of said electrodes comprising a metal electrode having a thin passivating material  
30 coating, wherein said passivating material is interposed between said electrochemically active material and said metal electrode, said

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electrochemically active material comprising an electrochemically active material in admixture with at least one polymerizable monomer; and  
polymerizing said polymerizable monomer to form a matrix which encapsulates said electrochemically active material.

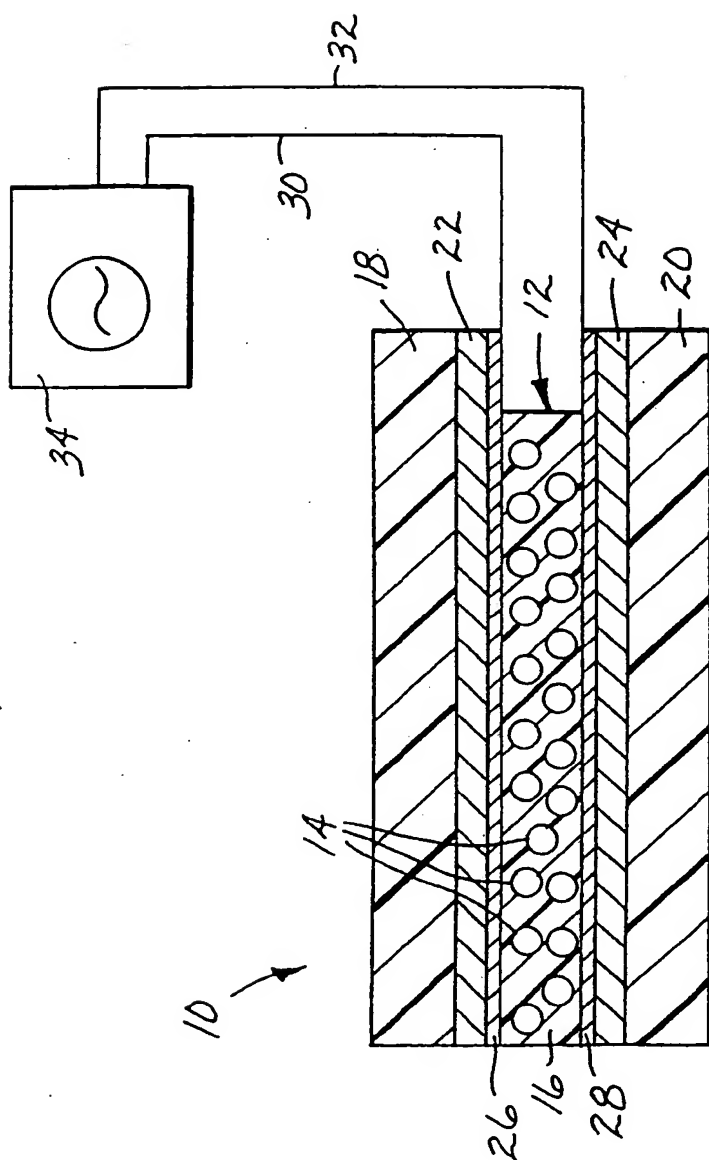


Fig. 1

## INTERNATIONAL SEARCH REPORT

PCT/US 92/10332

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 G02F1/1333; G02F1/1335		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	G02F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X Y A	DE,A,2 852 395 (BBC) 4 June 1980  see claims 1,2; figure 1 see page 7, paragraph 2 see page 7, paragraph 4 see page 11, line 26 - page 12, line 11 ----	1,3,5,8, 10 2,15 6,7,9, 14,16
X	DE,A,3 230 799 (LICENTIA) 23 February 1984 see claims 1,5 ----	1,6
Y A	EP,A,0 426 291 (UNIVERSITY OF HAWAII) 8 May 1991  see column 2, paragraph 1 see column 5, line 20 - line 23; figure 1A -----	2,15  14
<sup>10</sup> Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search  05 MARCH 1993		Date of Mailing of this International Search Report  10. 03. 93
International Searching Authority  EUROPEAN PATENT OFFICE		Signature of Authorized Officer  G. Lipp

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210332  
SA 67978

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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		JP-A- 3209425	12-09-91